Processes producing inner-valence shell vacancies in slow He^2 + CO collisions

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The method of Auger electron spectroscopy has been used to study the mechanisms responsible for the creation of inner-shell vacancies in He^2 + CO collisions at low impact energies (3 keV - 40keV). This experimental study follows recent observations by Folkerts et al. [1]. The fragmentaion of CO^{q+} was investigated at energies in the range 2 - 11 keV/amu. In addition tosingly and doubly charged residual target, a large fraction of CO^{3+} and CO^{4+} ions was observed. Because the projectile can capture only two electrons, the authors suggested that these Co^{q+} ions are produced after the capture of one or several inner CO electrons followed by an Auger process.

The figure one shows a typical Auger spectrum we obtained for the system He^2 + CO at an energy of 16 keV. Two groups of peaks are clearly distinguished. The group centered at ~ 35 eV originates from the deexcitation of He after a double capture into 2l2l' and 2l3l' excited states. The peaks located in the range 8-15 eV are due to the deexcitation of Co^{q+} (q equal to or larger than 1) [2] after the transfer of one or more than one inner-valence shell target electrons. With a detailed analysis of the collision system, we show that the above suggestion [1] has to be retained to explain the production of high charge states of the target. Nevertheless, other mechanisms such as Transfer-excitation can also be invoked to explain the observed peaks.

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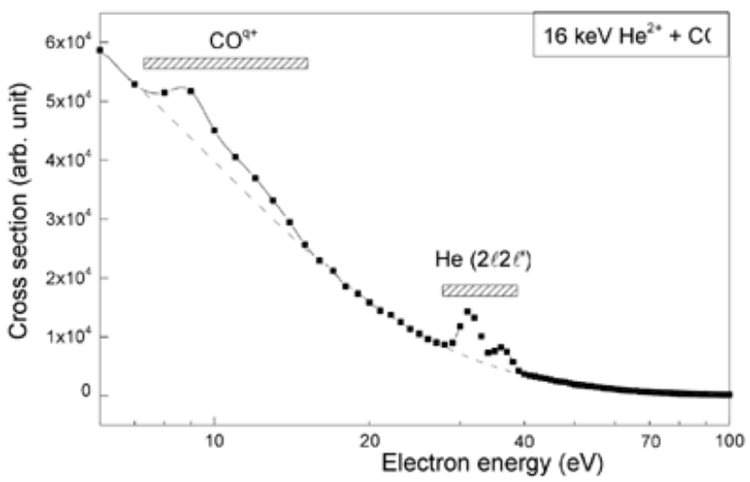

High Resolution Photoelectron Spectroscopy of Pu at the Advanced Light Source

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High resolution photoelectron spectroscopy of Pu has been performed at the Spectromicroscopy Facility (Beamline 7.0) at the Advanced Light Source in Berkeley. Based upon an initial analysis of the data, two key results are immediately obvious. (1) The 5d-5f Resonant Photoemission of the Pu 5f levels exhibits a dependence upon the Pu phase and structure. For example, the results from alpha and delta Pu differ significantly. This strongly suggests that electronic behavior is linked to atomic ordering and structure in Pu. (2) Contamination with oxygen and carbon may be more insidious and subtle than initially believed. Photoemission measurements at a photon energy of 800eV exhibit oxygen and carbon core level peaks, while the same sample shows no contamination utilizing a photon energy of 1253eV, a typical laboratory source energy used in ECSA machines (i.e., Mg k-alpha). In other words, what was thought to be “clean” may not have been. Furthermore, contamination issues like these have a crucial impact upon interpretation of Pu core level spectra, e.g. localized and delocalized screening by 5f electrons. Additionally, 5f-6p Resonant Photoemission, core level spectra (particularly the Pu 4f’s) and X-Ray absorption data, all from the Pu will be presented and discussed. Future plans, including ideas about studying magnetic effects in Pu, will also be described. This work was performed under the auspices of the U.S Department of Energy by Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48. Experiments were carried out at the Spectromicroscopy Facility (Beamline 7.0) at the Advance Light Source, built and supported by the U.S. Department of Energy.

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Local structure of self-organized uniform Ge quantum dots on Si(001)*

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Recent studies of electronic properties of self-assembled Ge Quantum Dots (QDs) on Si (001) produced by molecular beam epitaxy process have demonstrated the existence of discrete spectra of zero- dimensional hole states in the Ge clusters. Due to the 4% larger lattice constant and interatomic distances of Ge, strain evolving during growth of Ge films on Si(001) causes a series of critical morphological and some local spatial structure changes.

Spatial parameters of Ge atoms surrounding in Ge films on Si(001) produced by molecular beam epitaxy process were determined from Ge*K* EXAFS (extended X-ray absorption fine structure) spectroscopy data. XAFS measurements were performed at the VEPP-3 storage ring at the Budker Institute of Nuclear Physics in Novosibirsk. XAFS spectra were measured in surface sensitive mode based on total electron yield detection.

Electron diffraction and scanning tunneling microscopy results analysis revealed thickness of wetting layers (3-6 monolayer thick) and average meanings in plane dimension and height of the dots formed during strained layer epitaxy (Stranski-Krastanov growth mode). Two structures were formed in parallel on two part of Si(001) substrate. Both type of structure composed of three Ge/Si bilayers. The first type of the structure contains three pseudomorphous 4-monolayer Ge (2D) films and three blocking Si layers. The second structure type contains pyramid-like (3D) islands formed in Stranski-Krastanov growth in addition to the flat critical thickness 4,5-monolayer Ge films in order to reduce a high strain energy and blocking Si layers. This self-organized uniform Ge nanostructures have lateral sizes ~ 15nm and height ~ 1.5nm.

For analyzing the environment of Ge atoms Fourier–filtered EXAFS data were fitted with k and k^2 weighing in the range of photoelectron wave vectors from $2.5\approx^{-1}$ to $13\approx^{-1}$. The local microstructure parameters (interatomic distances, Ge coordination numbers and their anisotropy) are linked to nanostructures morphology and adequate models are suggested and discussed. It was established that pseudomorphous 4-monolayer Ge films, as it is called, contains at an average 50% Si atoms. Pyramid-like pure Ge islands formed in Stranski-Krastanov growth are characterized by interatomic Ge-Ge distances 2.41≈ (0.04 ≈ less than in bulk Ge) and Ge-Si distances 2.37≈. It was revealed that the pure Ge nanoclusters covered by 2-monolayer film with admixture at an average of 50% Si atoms impurity from blocking Si layers.

Elastic deformation spatial distributions in Ge QD on Si(001) and in their environment were obtained by valence force field (VFF) method. The values of Ge-Ge and Ge-Si interatomic distances obtained by processing EXAFS data within the limits of experimental error (±0.01≈) coincide with interatomic bond lengths obtained by VFF method calculation and allowed an understanding of previous capacitance spectroscopy results.

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Structure Of Heterometallic Complexes In The Hexane Extract On Modelling The Recovery Of Ruthenium From Radioactive Liquid Wastes*

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Extraction of ruthenium by trialkyl phosphine oxides ($(Oct)_3PO$) in the presence of copper has been detected. This phenomenon is explained by formation of heterometallic complexes in hexane solution. The composition and structure of the copper-ruthenium complexes in aqua solution and in the hexane extract were determined by XAFS spectroscopy. Local structure data for copper-ruthenium complexes in these solutions may be useful in the development of methods for the recovery of ruthenium from HLW (High Level Radioactive Liquid Wastes) and for separation of platinum metals.

Cu*K*, Ru*K* XAFS spectra of liquid copper-ruthenium systems in the hexane extract and aqueous solution were measured at the Budker Institute of Nuclear Physics in Novosibirsk.

To determine the character of the changes in the local environment of ruthenium and copper atoms the processing of the obtained spectral data was made using the EXCURV92 and FEFF7 packages. The fitting of the RuK EXAFS data for complexes was made for ruthenium atoms environment model including atoms of four NO_2 and one NO groups and the oxygen of the OH group taking into account multiple scattering effects. The accuracy of the interatomic distances determination did not exceed 0.01 Å in all fitting procedures.

Calculation of the XANES spectra with the FEFF7 package assuming a distorted square-planar environment of copper atoms has led to changes similar to those observed in the experimental spectrum. In such a system the coordination sphere of Cu could include three oxygen atoms of the PO groups of $(Oct)_3PO$ and one or two oxygen atoms bound to Ru.

It is shown that in aqueous solutions and extracts the $[Ru(NO)(NO_2)_4]^{2-}$ complex anion interacts with the copper cation which is hydrated or solvated by the (Oct)3PO molecules. The formation of a heterometallic complex increases the Ru–O (OH) distance from 1.96 to 1.99 Å. The local environment of copper atoms in the hetero-metallic complex $RuNO(NO_2)_4(OH)CuL_3$, L = $(Oct)_3PO$, in extract is represented by the $3O_1+O_2$ or $3O_1+2O_2$ models composed by three oxygen atoms of extractant and one or two oxygen atom of the Ru complex anion (one - from OH group) - in contrast to aqueous solution (4O- model). The environment of the copper atoms is also different in the extracts of the hetero-metallic complex and complex $[CuL_2(NO_3)_2]$ ($2O_1+2O_2$ environment model).

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A FLMTO study on ZnO's natural n-type conduction

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ZnO, a semiconductor with wide direct band gap of 3.37eV, has attracted much attention
because of its possible application in short-wavelength light-emitting devices. in order to develope such optoelectronic devices, one important issue that should be resolved is the fabrication of low-resistivity p-type ZnO. However, ZnO with a wurtzite structure is naturally an n-type semiconductor. Usually, this is attributed to the intrinsic defects O vacancies(Vo) and Zn interstitials (Zni). To find the exact contribution of Vo and Zni to the n-type conduction, the electronic structure of ZnO with Vo and Zni are studied using FLMTO method. The results show that due to the changes of interaction between Zn3d and O2p, the band gap of ZnO:Vo becomes bigger, and the Zn3d electrons are more local. However, impurity states appear just blow the bottom of conduction band in ZnO:Zni, indicating that Zni is partially responsible for the natural n-type.

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The kinetics of oxygen adsorption on Rh surfaces: a real-time Surface Core Level Shift study.

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During the last years, the study of the Surface Core Level binding energy Shift (SCLS) has provided a great amount of valuable information in surface science. The basic idea is that atoms that are inequivalent either from the chemical or the structural point of view have different binding energies of the same core levels. In this contest the combination of high photon flux and energy resolution now available at the synchrotron facilities permit to obtain new valuable information about the chemical and physical properties of metal surfaces. Particular emphasis is paid in describing the advantages of this method to study the kinetics of oxygen adsorption on the (111), (110) and (100) Rh surfaces. In fact a time resolution of 8 s/spectrum (Rh3d5/2 core level) with an overall energy resolution of 80 meV permits to follow in real-time the adsorption process. The development of new surface components at different coverage, ascribed to first-layer Rh atoms bonded with one or two oxygen atoms, permit to follow the formation of the different ordered structures and provides information on the electronic structure modification upon oxygen adsorption.

Cascading Decays of Vacancies in Atomic Inner Shells

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Creation of one or several inner-shell vacancies in an atom gives rise to a multi-step de-excitation cascade (a vacancy cascade) leading to multiple ionization of an atom due to consecutive non-radiative transitions. Starting from pioneering work by Carlson and Krause [1], most of the theoretical schemes used to describe vacancy cascades were based on the Monte-Carlo approach [2,3]. To calculate various characteristics of the vacancy cascades, we
proposed an approach based on the straightforward construction of de-excitation trees [4,5]. Within this scheme, the ion charge spectra [4-6], Auger spectra [7,8], and fluorescent spectra [9] for the cascades in rare gases are calculated. Combined calculation of ion yields and multiplet structures has made it possible to explain the new type of the photoelectron experiment - the Final Ion-charge Resolved Electron (FIRE) spectroscopy [10]. It is shown
that the dependence of the cascade development on the spin state of a decaying ion should be considered in accurate assignment of the 4d photoelectron spectra of rare earths [11].

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Yields of Multiply Charged Ions Produced by the Cascading Decay of Hollow Argon and Krypton Atoms

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Creation of a single inner shell vacancy in an atom produces a short-lived state liable to decay. A cascade of successive radiationless transitions produces multiply charged ions. The single-initial-vacancy cascade-produced ion yield spectra have been being studied since sixties [1]. If a greater number of inner-shell vacancies is created then the decay cascades become much more complex, and much higher stages of ionization can be reached. Such hollow states are exotic ones, and the studies on their decays are scarce. However, with coming fourth generation light sources the flux densities can be reached that could produce multiply inner-shell-ionized atoms with reasonable probabilities.

In this work we calculate the cascade-produced ion yield spectra of argon and krypton with two to eight vacancies in their K- and/or L-shells. The calculations are performed within a scheme described in [2]. Some results for krypton are presented in the figure. Both argon and krypton K-2 charge spectra are found to have double-peak structures due to the concurrence of radiative and non-radiative decay branches at the first step of decay. The argon L-n charge spectra represent almost pure single charge sates Arq+ with q=n+4. The L-n charge spectra of krypton have structures depending on the distribution of initial vacancies between L1- and L23- shells.

However, their overlap even for neighboring n is insignificant, therefore the charge spectra might be used to detect the production of specific hollow states.

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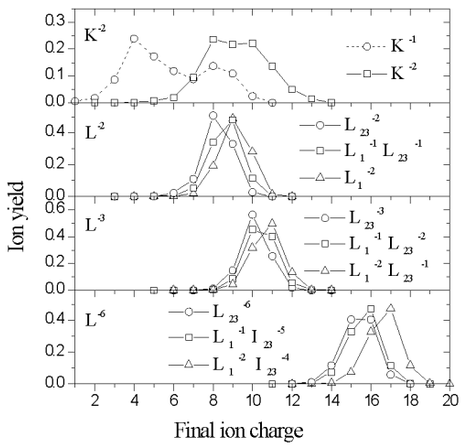

Orientation Effects in Anomalous Elastic Scattering of X-ray Photon by Linear Molecule

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Strong orientation effect is established theoretically upon the change of the scheme of supposed experiment on anomalous elastic scattering of linearly polarized X-ray radiation by the HF and HCl molecules near the *1*σ-shell ionization thresholds ($I_{1\sigma}$(HF)=694,10 eV, $I_{1\sigma}$(HCl)=2829,60 eV) and CO molecule near the *2*σ-shell ionization threshold ($I_{2\sigma}$(CO)=296.05 eV). Calculation of scattering amplitudes is performed including both the channels of single excitation/ionization and the virtual *shake-up*/*off* -type states of photoabsorption [1]. The calculation of the differential scattering cross section is performed for two schemes of the experiment. Scheme 1 (σ - π transition): molecular axis is perpendicular to the polarization vectors of incident and scattered photons, it has the same orientation as that of the wavevector of the incident photon and lies in the plane of scattering; scheme 2 (σ - σ transition): molecular axis is parallel to the polarization vectors of the incident and the scattered photons and it is perpendicular to the scattering plane.

Shown in the Figure are differential cross section of the scattering (θ is the scattering angle) of linearly polarised X-ray radiation by the CO molecule: [σ - π] - scheme 1; [σ - σ] - scheme 2. Single excitation/ionization approximation results are shown with squares.

It follows from Figure that upon going from scheme 2 to scheme 1, an additional broad intensive elastic scattering resonance appears in the long-wave region of theoretical spectrum. Inclusion of the *shake-up*/*off*-type channels substantially refines the results of the single excitation/ionization approximation.

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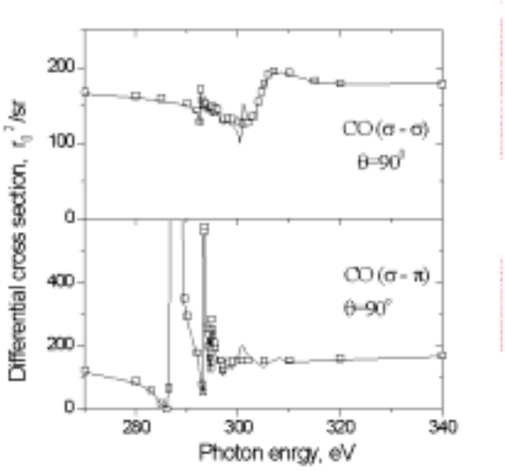

Processes of Multiple Ionization in Inner Shell Photoabsorption of Some Diatomics

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The spectra of multiple ionization of the CO and N_2 in the gas phase in the region of the *1s*-shell ionization threshold of C and N are studied theoretically. The processes of additional ionization from *1π*-, *4σ*- and *5σ*-shells are included. The calculation of one-electron wavefunctions is carried out with inclusion of the effect of core relaxation in the field of the inner shell vacancy within one-centre method in the Hartree-Fock (HF) approximation. The energies and wavefunctions of the terms for the excited configuration were obtained after solution of secular equation by the method [1]. The study of the effect of configuration interaction (CI) on energy position and extension of the multiplet structure of the states of multiple excitation/ionization is performed for the configuration $2\sigma^{-1}1\pi^{-1}2\pi^{1}$ in CO. In this work we studied only the effect of correlations phenomena on the magnitude of *1π-2π* electron-electron interaction which determines the extension of $2\sigma^{-1}1\pi^{-1}2\pi^{1}$ configuration multiplet structure. Principal correlations leading to the decrease of multiplet extension are described by excitation of σ-symmetry core electrons into virtual states of σ-symmetry, with simultaneous filling of *1π*-vacancy by *2π*-electron, as well as by excitation of *1π*- and *2π*-electrons into virtual states of π-symmetry. Cross sections are calculated by the methods of the theory of non-orthogonal orbitals. The electron spectra connected with the formation of terms $2\sigma^{-1}1\pi^{-1}2\pi^{1}(^{1}\Sigma^{+})$ are compared in the Figures with the experimental results (squares) from [2,3]. Calculations of the intensities of transitions are performed in length (solid line) and velocity (dashed line) forms of the dipole transition operator.

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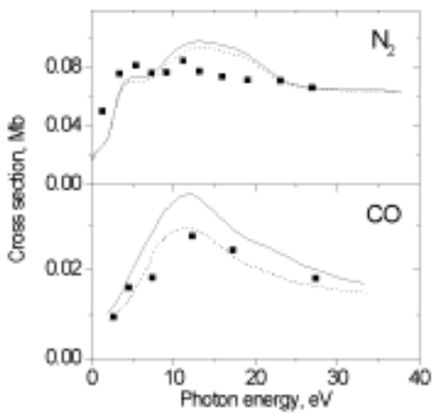

TEM-EELS Investigations of Nanoscale Multilayers in the Linescan Mode*

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The motivation for investigations of nanoscale multilayers is their expanding importance in materials science. For some years, one of the examples for new applications of metallic layers has been Giant Magneto Resistance (GMR). For understanding this effect and in order to optimize GMR-based devices the knowledge of the nanostructure including the elemental distributions is essential. In particular, the degree of mixing of nanoscale Co/Cu multilayers was the focus of interest. These elements are immiscible in the bulk but this may be completely different in the case of nanoscale layers, as shown by Pelton [1]. In this contribution, analytical electron transmission microscopy has been used to check this point. A stronger mixing of multilayers produced by pulsed laser deposition compared with those deposited by sputtering could be shown by means of EELS intensity profiles along cross sections of Co/Cu multilayers with single layers thicknesses of 2 to 16 nm [2].
The EELS profiles were obtained in a TEM with a STEM unit in the linescan mode. For experimental optimization the following parameters were investigated: the spot size of the electron probe, the electron microscopic specimen thickness, the number of pixels along the line, the dwell time per pixel, the tilt between electron beam direction and multilayer interfaces and any specimen drift. Furthermore, calculations provided evidence that an instrument with a field emission gun is necessary for acquiring the intensity profiles on cross sections of nanoscale multilayers. The experimental results were confirmed by energy filtered imaging and by Auger electron spectroscopic investigations.

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Manifestation of Strongly Delocalized Atomic States in the Photoionization Cross Sections of Ar, Kr and Xe in the Vicinity of the Subvalence *n*s- Shell Threshold

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Recently [1], the manifestation of the strongly delocalized doubly-excited atomic states having an outer *n*f-electron (*n*f-resonances) was observed and calculated in the near-threshold Xe 5s-photoionization cross section (PI c.s.). It was obtained that the *n*f-resonances are visible in spectra only if their wave functions strongly overlap and are mixed with the wave functions of the doubly-excited atomic states having an outer *n*p-electron (*n*p-resonances).

Similar manifestations of the *n*f-resonances in the PI c.s. of Kr and Ar atoms were studied. The Kr 4s- and Ar 3s- PI and the total photoabsorption c.s. were measured in the vicinity the subvalence *n*s-thresholds by means of photon-induced fluorescence spectroscopy using the synchrotron radiation of the electron storage ring BESSY I, Ber-lin. The exciting-radiation bandwidths were 2 meV in the Kr case and 4.8 meV in the Ar case. The measured PI c.s. exhibit many resonances caused by the excitation and autoionization decay of the doubly-excited atomic states.

The *n*s- PI and total photoabsorption c.s. were also calculated using many-body perturbation theory and configuration interaction techniques. Calculations were performed in two approximations: with inclusion of the *n*p-resonances and with inclusion of both the *n*p- and *n*f-resonances. Comparison of the measured and calculated 4s-PI and total c.s. of Kr in the vicinity of the 4s-threshold (see figure) reveals that the *n*f-resonances manifest themselves as a single separate resonance at 27.607 eV in both the 4s-PI c.s. and in the total absorption c.s. One can propose that it corresponds to the measured resonance at 27.600 eV. The experimental resonance at 27.600 eV has a profile which differs from other near-threshold resonances, and its shape was reproduced in the calculated total absorption c.s. but not in the 4s- PI c.s.

In the Ar case the *n*f-resonances are located near the third prominent $3p^4 4s5p$-resonance (31.624 eV) in the 3s-PI c.s. [2]. Our calculations predict a relatively small manifesta-tion of the *n*f-resonances in the Ar case because of two main reasons:

-the smaller admixture of wave functions of *n*p-resonances to those of *n*f-resonances;
-the small *n*f-resonances are blended by the prominent resonance mentioned above.

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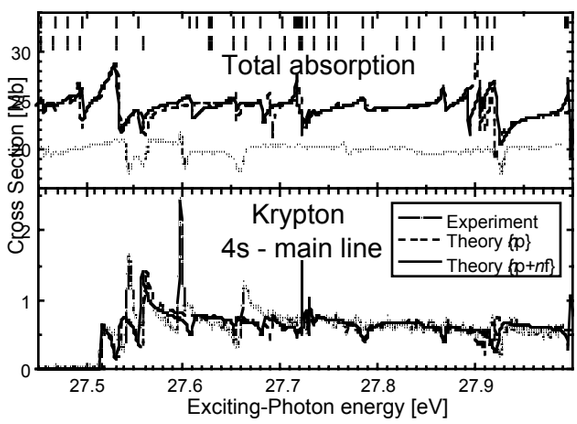

CIRCULAR DICHROISM IN TWO_ELECTRON CONTINUA

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Double photoionization by circularly polarized light, and electron impact ionization of laser excited and orieted atoms have been investigated theoretically.We have found a strog dependence of the angular correlation an the energy distribution onthe light helicity. Our calculations show in particular that the dichroism depends sensitively on the choice of double continuum wave functions. The observation of this dichroism constitutes therefore a sensitive test for electronic correlations involved. Our numerical results compare favourably with accurate experimental data.

EXACT ASYMPTOTIC BOUND STATE WAVE FUNCTIONS FOR ATOMS

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Asymptotic forms of helium wave functions have been reported several times in the literature. In our opinion all these previous treatments are either incomplete or wrong. This paper derives here for the first time in a systematic way expressions for atomic wave functions in the limit where all mutual particle separations are large.Of course, we rediscover exponential tails. But these tails are modified by correlation. And these modifications have been calculated in Eikonal approximation which is exact for Coulomb forces. The problem can be solved for any atom. The mathematical technique as well as results compared with previous work will be presented at the conference.

Inner-Valence Ionization of Weakly Bound Molecular Clusters and Efficient Relaxation by Electron Emission

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Recent theoretical investigations accompanied by large-scale ab initio computations[1-3] were devoted to the question how molecular clusters relax that have been excited by inner-valence ionization. For water clusters, for instance, electron emission dominates the overall relaxation behavior, taking place on the femtosecond time scale. The occurrence of this newly discovered process in such a relatively low-excitation regime may be surprising, particularly in view of the fact that isolated, inner-valence excited H_2O^+ cations can dissipate their excess energy only by vibrational motion and photon emission. Hence, the nature of the electronic decay process taking place in cationic clusters is intermolecular.

The following, simplified picture has emerged. Ionization out of an inner-valence orbital leads to the formation of a hole which is localized at one of the monomers constituting the cluster. An outer-valence electron at this cationic monomer can drop into the inner-valence vacancy. Due to an extremely efficient coulombic mechanism, which will be discussed in the presentation, the released energy is transferred to neighboring monomers. In this way, an outer-valence electron is ejected in the molecular environment of the initial cation. The resulting final states are characterized by two positive charges distributed over two or more monomers. Thus, coulomb repulsion of the two holes is reduced, which explains the energetical accessibility of electronic decay channels. We would like to emphasize that for the systems we studied, inner-valence excited cationic monomers without a cluster environment are electronically stable.

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Angular Distributions of Resonantly $3d^{-1}np$ (n = 5, 6, and 7) Excited Krypton

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Auger angular distributions provide a very sensitive tool in studying correlation effects in many-electron atoms. So far, such distributions were mainly explored after an initial resonant excitation of a inner--shell electrons into one of the unoccupied valence shells. While a detailed analysis of the angular dependence and its comparison with theory was first hampered by the low resolution of the observed electron spectra, recent improvements have made it possible to distinguish many of the finally populated states.This facilitates the test of different theoretical models without the need to average over closely separated Auger lines.

A theoretical study of the angular distribution parameters for resonantly-excited krypton will be presented. Excitations of one of the $3d_{3/2,\ 5/2}$ electrons into np shells with principal quantum numbers n = 5, 6, and 7 are considered along with a subsequent MNN spectator decay of these 'intermediate' states. Calculations within the multiconfiguration Dirac-Fock model confirm - as already observed by Farhat et al. [1] - that the spectator-core coupling becomes less important as the electron is excited into subshells with large(r) n. Also, the spectator decay is often accompanied by shake-processes owing to the rearrangement of the bound-state density and the different potentials as seen by the valence electron. We will discuss the effects of relativity and correlation on the angular distribution of krypton and present computational tools [2] which, for the first time, enable us to include electron--electron correlations systematically as has been possible for radiative decay processes for several years already.

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Theoretical investigations on relativistic, correlation, and relaxation effects in the spectra of Cu II

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The spectra of Cu II has been a focus of interest during recent years. A profound knowledge of these spectra is not only useful for plasma diagnostics but also for the development of copper vapour lasers and measurements of Cu abundances in interstellar HI clouds. Therefore, a large number of measurements and calculations have been carried out over the years in order to explore the level structure and lifetimes of Cu^+ ions [1,2]. But yet, both the theoretical and experimental results still scatter quite remarkably and, thus, need further exploration.

Here, we will present a detailed ab-initio investigation on the structure and the decay branches of the low-lying levels of Cu^+ ions. Multiconfiguration Dirac-Fock wave functions [3,4] were applied to deal with the (dominant) effects of relativity, correlation, and the rearrangement of the electron density within the same computational model. With the help of systematically-enlarged wave function expansions we are able to monitor the convergence behaviour of excitation energies and lifetimes as the size of the expansions increases. Our results show a significantly better agreement with experiments [1] and demonstrate the capabilities of carefully designed ab-initio studies. Apart from the electric-dipole (E1) allowed transitions among the $3d^{10}$ - $3d^9$ 4p and $3d^9$4s - $3d^9$ 4p configurations, we investigate and present 'forbidden' E2 transition probabilities and lifetimes also for the metastable $3d^9$ 4s even-parity levels. Similar investigations are presently carried out for several adjacent spectra in the Cu II isoelectronic sequence.

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Relativistic Studies on the Electronic Structure and Properties of Open-Shell Atoms*

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The difficulties in studying open-shell atoms and ions have long been underestimated. The first (successful) structure calculations of a few selected atoms in the sixties and seventies namely enhanced the belief, that it would take only a bit more effort and computational power, to theoretically predict the structure and properties of atoms in rather arbitrary configurations. Today we know, however, that many properties are very sensitive to the electronic motion and, therefore, critically depend on the shell structure of the system. That is why most of the open-shell atoms are yet not well understood quantitatively even though much larger computations are nowadays feasible.

This contribution gives a brief status report on the calculation of open-shell atoms and ions. I will discuss, in particular, the capabilities and applications of the RATIP program [1] for calculating (relativistic atomic) transition and ionization properties. This package has developed into one of the main atomic structure programs within the last years. It is based on multiconfiguration Dirac-Fock wave functions [2] and, thus, may incorporate all dominant effects of relativity, correlations, and of the rearrangement of the electron density within the same computational model. By using an object-oriented design, the present version of RATIP starts a new generation of atomic structure tools which will surely be found useful in the years to come.

RATIP supports large-scale computations on a variety of properties including the interaction of atoms with the radiation field and atomic processes with one electron in the continuum. A number of case studies which were carried out in this environment include accurate calculations on Einstein coefficients, branching ratios, lifetimes as well as Auger intensities and angular distribution parameters [3]. I will demonstrate the main features of RATIP for a few simple shell structures but also for those in which many-particle effects have to be treated more systematically.

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AN ANGULAR CORRELATION FUNCTION FOR DOUBLE PHOTOIONIZATION IN ATOMS

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We consider the successive emission of two electrons following the absorption of a photon by an atom. An expression for the angular correlation between the two photoelectrons is derived in terms of the angle between their directions of propagation, following the generalized approach of Biedenharn and Rose [1].Our theory treats double photoionization as a tow-step process and does not refer to perturbation theory. The dynamics of the process are embodied in the reduced matrix elements. It is clear that the angular correlation is closely related to the properties of the angular momenta. A sample computation is made for double photoionization in argon leading to the 3p$^-2$ ^{1}D^e final ionic state.

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Excitation of plasmons of anisotropic nanostructures by nearby electrons

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Following the discovery of the fullerene molecules, multishell fullerenes and nanotubes have been produced with carbon, boron nitride, and other planar uniaxial materials. These particles typically have a few tens of nanometers size and present a peculiar "in-shell" anisotropy and an hollow inner cavity. We have developed a dielectric formalism and discrete dipoles approach (DDA) for the resolution of Maxwell equations taking account of these peculiarities[1]. In the present contribution, we will emphasise the consequences of the anisotropy on the surface modes of the nanoparticles. In particular, the multi-peak structure of the surface modes will be analyzed as a function of the anisotropy.

Comparison of simulations with Electron Energy Loss Spectroscopy (EELS) experimental data shows [2] (i) that the model can be successfully applied. In particular, two surface modes at 13 eV and 17-18 eV (in carbon compound) and at 12 eV and 16 eV (in BN compound) are clearly associated with out-of-plane and in-plane resonances of planar crystals. (ii) The shift of the modes with respect to the impact parameter is analysed in terms of the multipolar decomposition of the Coulomb field of the electron. (iii) The width of the shell is shown to affect the relative intensity of the "in-plane" and "out-of-plane" modes.

Recent optical data obtained on dense packed films of spherical multishell fullerenes [3] are also analysed within the same framework. Consequences on the possible presence of fullerene-derived particles in the interstellar dust [4] are drawn.

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Photoelectron Spectroscopy of Pristine and Cs-Intercalated Single-Walled Carbon Nanotube Bundles

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The work functions and the electronic structures of pristine and Cs-intercalated single-walled carbon nanotube (SWNT) bundles were investigated by photoelectron spectroscopy using both synchrotron radiation light and an He discharge lamp. The work function of pristine single-walled carbon nanotube bundles having an average tube diameter of 1.4 nm was found to be 4.8 eV, which is about 0.2 eV larger than that of graphite. A drastic decrease of the work function to about 2.0 eV was observed in the Cs-intercalated sample [1]. The result suggests that Cs-intercalated SWNTs should have a lower electron emission threshold field than that of the pristine material. The valence band states of the pristine bundles were considerably altered from those of graphite because of the nanometer scale tubular structure. A spectral shift to the higher binding energy side and a considerable increase of photoemission intensity at the Fermi level, indicating a charge transfer from Cs to C, were clearly observed in the Cs-intercalated bundles. The high-energy resolution C 1s spectrum of the pristine SWNT bundles showed a considerably broader peak (FWHM: about 0.6 eV) than that of graphite (0.3 eV). At least, some of the nanotubes had to be metallic because the C 1s peak showed the Doniach-Sunjic type asymmetry.

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Photoemission electronic states of La$_1-x$Ca$_x$MnO$_3$

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The X-ray photoemission (XPS) from the La-3d,4d, Ca-2p, Mn-2p, Fe-2p, Tb-4p and O-1s core-levels as well as the ultraviolet photoemission (UPS) from the valence band of the CMR mixed-valent manganates have been studied. The spectra have been measured in metallic ferromagnetic state at 80K and insulating paramagnetic state at 300K for the samples of: La$_0.63$Ca$_0.37$MnO$_3$ with T$_C$ = 270K, La$_0.63$Ca$_0.37$Mn$_0.92$Fe$_0.08$O$_3$ with T$_C$ = 170K and (La$_0.57$Tb$_0.10$)Ca$_0.33$MnO$_3$ with T$_C$ = 160K. The core-level spectra for all compounds are essentially the same as far as their FWHM and energy positions of 2p-, 3d- and 4d-lines are concerned. From the Mn-2p spectra and their comparison with the relevant Auger spectra [1] values of the charge transfer energy delta, the hybridization energy between Mn-3d and O-2p states t and the on site Coulomb correlation energies U$_pp$ in Mn 3d and U$_pp$ in O 2p states were estimated to be about 4 eV, 3.8 eV, 3.5 eV and 6.7 eV, respectively. The analysis of Mn 2p spectra shows a mixed character of the ground state with almost equal contributions from Mn$^3+$ d^4(t^3$_2g$e^1$_g$; S=2) and (t^3$-2g$e^2$-g$L^1; S=2) states as well as with contributions from Mn$^4+$ d^3(t^3$_2g$; S=3/2) and (t^3$_2g$e^1$-g$L^1; S=3/2) states corresponding to the hole (L) doping concentration. The O-1s core-level spectra exhibit an asymmetry toward the higher binding energies and show a higher binding energy shoulders. The valence band spectra at 300K for the undoped and the Fe-doped La$_0.63$Ca$_0.37$MnO$_3$ specimens are very similar showing a two-peak structure at about 3.4 eV and 5.6 eV below the upper edge of valence band and a band gap some tenth of eV. Comparing our spectra with the high resolution spectra obtained with 110 eV synchrotron radiation [2] we conclude that the two peaks are very characteristic for transition metal compounds revealing a signature of partially hybridized Mn 3d - O 2p states contributing to the valence band. In contrast, the valence band spectrum of Tb doped specimen shows a third peak most likely coming from the 4f Tb states and giving rise to the density of states at higher binding energy part of the band. An analysis of the relative changes of density of states in the gap near the band edges as a function of temperature in metallic ferromagnetic state at 80K and insulating paramagnetic state at 300K shows that the effect of temperature is very small. The results are compared with the Nuclear Magnetic Resonance study on ^{55}Mn and ^{57}Fe which shows that Fe ions have the valency 3+ which should result in a shift of the Mn average valency 4+ upon Fe doping.

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XPS Study of Antimony Segregation at Germanium Surface

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The equilibrium segregation of antimony at germanium surface has been investigated using X-ray Photoelectron Spectroscopy (XPS). Heat treatments of various durations have been carried out under vacuum at T=600ºC. In-situ experiments were performed using a heating cell attached to the XPS electron spectrometer. Both chemically polished and argon sputtered surfaces were studied. The argon sputtering prior to the heat treatment enhances drastically the segregation process. The results show an increase of the Sb/Ge ratio from zero to 5% at Ar-sputtered surface as the duration of the heat treatment increases from zero to 800 minutes. Furthermore, two new XPS peaks appear in the Ge3d region, at 32eV (S1) and 33.5 eV (S2) binding energies after 1 hour treatment. The ratio of the peaks intensities S2/S1 is 0.63. XPS measurements performed at different angles show a strong variation of the bulk Ge3d signal while S1 and S2 remain quasi constant, suggesting that these two peaks are surface related.

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Separation Dynamics of a Luminescence from Raman Scatterings in Characteristic X-Ray Radiation Processes of Y Compounds

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The electronic relaxation dynamics that separates a luminescence from Raman scatterings is theoretically studied in the characteristic x-ray radiation processes of Y compounds. In the recent years, the characteristic x-ray radiation spectra have been experimentally observed in detail for various insulators. Especially, in Y compounds(YF_3 and YCl_3), the characteristics of these radiation spectra are as follows[1]. When the incident photon energy is below the absorption edge, resultant radiation spectra have two peaks whose energies depend linearly on the incident one. On the other hand, when the incident energy is above the edge, radiation spectra separate into three peaks; one peak whose energy is fixed, and the two peaks whose behaviors are the same as mentioned before, in its higher energy side. The absorption spectra relevant to this photoexcitation have one sharp peak with a tail in its higher energy side. This characteristics of the absorption spectra can be explained by the one-body picture in which a core electron is excited into two different conduction bands. However, the three-peak structure in the radiation spectra cannot be explained by such a one-body picture. While, we consider a many-body problem in a four-band model composed of dispersionless deep, shallow core bands and conduction and valence bands. The Coulomb interactions among the conduction electrons and the valence holes are taken into account by the perturbation theory. In our model, the tail in the absorption spectra is due to new conduction electron-valence hole pair creation through the Coulomb interaction. In the radiation spectra, the peak whose energy is fixed, is due to the luminescence which occurs after the electronic relaxation that the newly created electron-hole pairs go away from the original sites where they were created. The other two peaks are considered as Raman scattering peaks. In one of these final states, only one electron remains in the conduction band. While, in the other final state, one conduction electron remains together with one conduction electron-valence hole pair. With this model, the experimental results have been well-explained.

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Electronic structure of self-assembled organic/inorganic semiconductor interfaces: lead phthalocyanine on InSb and InAs(100)c(8x2) as well as Si(111)root3xroot3R(30°)-Ag

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Organic-inorganic semiconductor heterostructures present a major interest for their potential applications in electronics, optoelectronics, sensors and biochips. In the monolayer regime metallo-phthalocyanines, a most important class of organic molecules, deposited under ultra high vacuum onto the In rich, c(8x2) reconstructed, InAs and InSb (100) surfaces as well as on the silver terminated Si(111) surface (presenting a root3xroot3R(30°)-Ag reconstruction) form ordered superstructures [1-3]. We have followed the evolution of the electronic properties of the lead-phthalocyanine (PbPc)/InSb,InAs(100)c(8x2) and Si(111)root3xroot3R(30°)-Ag interfaces during their formations by high resolution synchrotron radiation photoelectron spectroscopy (valence bands and core levels). In contrast to previous results on metallic substrates [4] the organic macrocycle preserves its integrity upon chemisorption even if the central lead atom migrates away upon annealing. We especially focus on the modification of the monolayer excitonic structure directly related to the shift of the highest occupied molecular orbital (HOMO) and the filling of the substrate band gap with new electronic states.

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X-Ray Absorption Near Edge Structure Studies of Fe1-xNixOy Thin Films

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In a previous paper [1] we reported the studies of Fe and Ni L-edge x-ray absorption near edge structure (XANES) measurement of a series of $Fe_{1-x}Ni_xO_y$ ($0<x<0.71$) spinel thin films grown by oxygen plasma assisted MBE. The results indicate that the caion distribution in these thin films is dramatically different from the bulk samples. For $x<0.5$, Ni replaces the trivalent and the divalent Fe from the tetrahedral and the octahedral sites, respectively, with a ratio of 1:2. At $x=0.5$ all the divalent Fe are replaced by Ni ions. Further, for $x>0$, replaces the trivalent Fe at tetrahedral and octahedral sites up to $x=0.71$. In order to study the valence state of the caions in these thin films we have performed Fe and Ni K-edge XANES studies of the same series of Fe-Ni-O spinel thin films. The transition metal K-edge x-ray absorption spectra provide information about the valence state of the absorbing atoms. Our results show that the variation of Fe valence is consistent with the structural studies reported in Ref. 1. While the valence of Ni does not dependent on the Ni concentration. In order to keep the charge balanced, for x greater than 0.5, a ligand hole must be created [2].

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Observation of back-donation in 3d metal cyanide complexes through NK absorption spectra

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The 3dπ-2pπ* charge transfer (back-donation) between the 3d atom and ligand atoms is a characteristic feature of chemical bonding in complexes with ligands CN-, CO, NO, etc. having low-lying unfilled antibonding molecular orbitals (MOs) of π symmetry (2pπ*) [1]. Electronic structure of cyano complexes was extensively studied by X-ray absorption, but only the spectra of 3d atoms at the K and $L_{2,3}$ edges are known in the literature, while no investigations of ligand core excitations are available. The present study is aimed to investigate and discuss X-ray absorption spectra of ligand and 3d-metal atoms for a series of cyano complexes in order to obtain information on their electronic structure and the back-donation effect in the 3d atom-ligand bonding. The X-ray absorption measurements on cyano complexes were mainly performed at the SX 700-I monochromator (BESSY I) in the total electron yield mode. From the comparison of NK absorption spectra for cyanide anion CN^- in HCN [2] and cyano complexes (Figure) it is obvious that the spectra of some complexes show an extra lower energy π band t: it is absent in spectra of $Co(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ with the $3d^6$ electronic configuration of a metal atom. The observation of the band t in NK absorption spectra of hexacyano complexes having the partially filled upper valence MO $3dt_{2g}$ is the direct experimental evidence for the $3dt_{2g}$– 2pπ* bonding (the back-donation effect) in these complexes.

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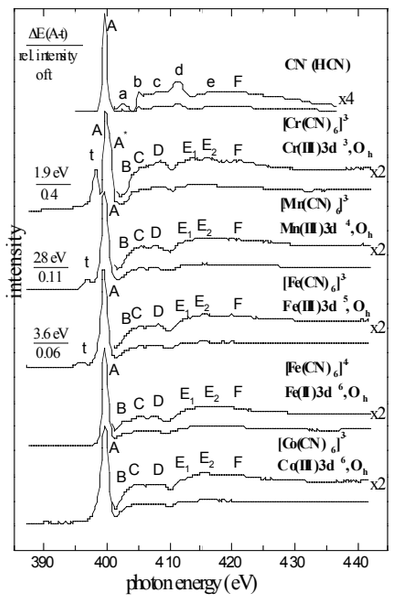

Modification of Polyolefins with Silicon Copolymers: Processing, Bulk and Surface Properties

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Polydimethylsiloxane (PDMS) containing copolymers display an unusual combination of properties like low glass-transition temperature, low surface energy, good thermal and UV resistance, biocompatibilty, etc. When small amounts (1-5 %) of PDMS containing copolymers are mixed with various linear organic polymers or incorporated into the structures of network polymers, they tend change the surface properties without influencing the bulk morphology and the properties of the base resin. We have used two different types of PDMS containing block copolymers (a triblock copolymer and a multiblock or segmented copolymer) for the surface modification of polyetheylene and polypropylene. Blends were prepared using a twin-screw extruder and characterised using XPS and IR spectroscopic and thermal (DCS) techniques. Influence of the additive type, additive level and PDMS segment molecular weight in the additive, on the processing conditions as well as surface and bulk properties of the resulting system will be presented.

Deposition and Stability of Metal Ions on Oxidised Silicon Surfaces: Electrochemical Correlations

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Electrochemical, chemical (electroless) and physical (vapour) deposition of metals and their corresponding ions of V, Cr, Mn, Co, Cu, Ag, Au, Pt, Pd, etc. on to various surfaces are important in fields involving coatings, semiconductors, solar energy applications, catalysis, etc. Recent developments in scanning microscopic techniques have enabled the researchers to manipulate the deposition of some metals/ions also for nanoscale applications. Fundamental questions governing these processes and related to the chemical/electrochemical properties of the metal ions and the corresponding substrate surfaces are still subject of some debate. In this context, we have used the XPS for characterisation of the chemical state of the metals and the ions deposited via electrochemical and/or electroless methods on to thin and oxidised surfaces of Si. An attempt to establish correlation of the stability of the certain oxidation states with their electrochemical and other thermodynamical parameters will be presented.

**One-body Green's Functions of Half-filled Hubbard Models,
Predominance of Multi-magnon Incoherent Component and Minuteness of Zero-magnon Coherent one**

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For one- and two-dimensional half-filled Hubbard models, we show that multi-magnon incoherent component predominates the Lehmann spectrum of the one-body Green function, while zero-magnon coherent component makes only a minute contribution to the spectrum. The one-body Green functions are calculated by a quantum Monte-Carlo simulation. Since a collective spin excitation, a magnon, is gapless in the simple Hubbard model, the multi-magnon incoherent component, which reflects coupled states of an electron(hole) and magnons, inevitably overlaps the zero-magnon coherent one. As a result, coherent and incoherent components can not be distinguished clearly from each other in this model.

To overcome this problem and distinguish the coherent component from the incoherent one in the Lehmann spectrum, we artificially add a site-diagonal staggered potential Δ to the Hubbard models. Due to this Δ, an energy gap opens in the magnon excitation and, as a result, the coherent component is well separated from the incoherent one. Quantitative analysis on the Δ-dependence of these two components shows that the weight of the coherent component is less than a few percent in the limit of Δ_0, which corresponds to the simple Hubbard model. This means that it is the incoherent component which predominates the Lehmann spectrum, while the coherent one makes only a minute contribution. In contrast to the widely accepted band theory, our results indicate that a peak in the photoemission spectrum of an insulator driven by the strong Coulomb repulsion does not correspond to a one-electron state, since this peak originates mainly from the incoherent component.

Chemical-Bonding-State Analysis of Oxygen on Graphitic Surface in Microporous Carbon by Soft X-Ray Spectroscopy

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Microporous carbon has been widely used as both an adsorbent and a catalyst in various industrial fields: in water treatment to remove organic pollutants from water and in air pollution sensors to concentrate the pollutants [1]. Its adsorbent and catalytic characteristics strongly depend on the chemical state of its graphitic surface, especially on the chemical bonding states of oxygen in the micropores. However, oxygen in microporous carbon has rarely been directly observed, and its chemical bonding states are not clearly understood, because of the technical difficulty of in-situ direct observation of molecules in a bulk matrix. In order to directly observe molecules in bulk microporous materials, one needs to use spectroscopic methods that have bulk-sensitivity, high-resolution, and high-efficiency. One suitable method is soft x-ray emission spectroscopy using highly brilliant synchrotron radiation, because of the longer transmission length of soft x-rays in solid matter.

The aim of our work therefore is to directly observe oxygen in microporous carbon using soft x-ray emission and absorption spectroscopy, and to determine its chemical bonding states. We measured soft x-ray emission and fluorescence yield (FY) absorption spectra of microporous carbon in the OK region using highly brilliant synchrotron radiation at the Advanced Light Source (ALS). OK x-ray emission and FY absorption spectra of commercially obtained microporous carbon were measured using a grating x-ray spectrometer installed in beamline BL-8.0 [2]. Comparing these x-ray spectra with calculated O2p-DOS (density of states) of simple model clusters composed of a graphitic cluster (C24H11) bonded with typical substituents such as –OH, -COOH, and –CHO, we conclude that the measured x-ray spectra cannot be explained by these typical substituents on the graphitic surface. Further theoretical analysis of these x-ray spectra is in progress to determine the chemical bonding states of oxygen in microporous carbon.

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Characterization of semifluorinated alkanethiols on Au and Ag metal surfaces by XPS, IRRAS and NEXAFS spectroscopy*

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Self-assembled monolayers (SAM) are close-packed arrays of chain- or rod-like molecules which are chemically anchored to a suitable substrate. The outer surface of a SAM is constituted by a tail group. Providing that the tail group has a strong polar character or is sufficiently large it can not only determine the properties of the outer film surface but also significantly affect its entire structure. One of such systems are semifluorinated alkanethiols (SFAT) $CF_3(CF_2)_9(CH_2)$nSH (F10HnSH: n = 2, 11 and 17), where the hydrocarbon chain of alkanethiols is terminated by a fluorocarbon chain. The physical and chemical properties of the fluoro- and hydrocarbon chains are different, which stems from a larger atomic volume and higher electronegativity of fluorine as compared to hydrogen. We have studied the structure of SFAT on Au and Ag by X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRRAS), and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. This SFATs were found to form highly ordered and densely packed SAMs on both substrates. The molecules are strongly bonded to the substrates via their sulfur head groups, in the same manner as conventional alkanethiol (AT) SAMs. The hydrocarbon (except for n = 2) and fluorocarbon parts of the adsorbed SFATs retain the expected planar zigzag and helical conformations of the respective bulk materials. The orientation of the fluorocarbon chains do not depend on the substrate. These entities are almost perpendicular to the substrate in F10H2S/Au and F10H2S/Ag and become slightly more tilted in SFAT SAMs with longer hydrocarbon moieties. The alkyl part of the SFAT films exhibits very similar tilt and twist angles as the pure alkanethiols on Ag and Au substrates. Considering the reduced van der Waals interaction between the hydrocarbon chains in the SFAT films as compared to neat AT SAMs, the substrate-related differences in tilt and twist angles for both systems appears to be predominantly associated with the different character of the head group-substrate bonding on Au and Ag.

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Modification of alkanethiolate monolayers by low energy electron irradiation: A combined NEXAFS and XPS study*

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The damage produced in thin organic films by light and X-ray photons can be essentially related to the low energy secondary electrons arising through the inelastic scattering of the primary electrons created within the photoemission process. The excitation of electrons in antibonding molecular orbitals and ionization of particular molecular groups mediated by these electrons result in a cleavage of individual molecular bonds with the subsequent partial desorption and chemical modification of the irradiated film. This low energy electron induced damage has been studied in self-assembled monolayers (SAM) of alkanethiols (AT) and monitored in-situ by X-ray photoelectron spectroscopy (XPS) and angle resolved near edge X-ray absorption fine structure (NEXAFS) spectroscopy. For the fundamental understanding and evaluation of individual electron-induced processes we varied the noble metal substrate as well as the length and isotopic composition of the AT chains. Additionally we have substituted the terminal methyl group of conventional AT by a perfluorodecyl chain. All investigated systems exhibit qualitatively similar behavior with respect to low energy electron irradiation. Both the hydrocarbon and the fluorocarbon parts and the S-Au interface are affected simultaneously through the electron-induced dissociation of C-H, C-F, C-C, C-S, and Au-thiolate bonds and appearance of conformational and orientational defects. These processes result in progressive disordering of initially well-ordered, densely packed SAMs, desorption of film constituents, reduction of pristine thiolate species, the appearance of new sulfur species and C=C double bonds. In general we deduced for all alkanethiol-like monolayers (i), whereas the entire SAM is damaged, the film-vacuum interface is predominately affected by irradiation-induced desorption processes, (ii) the desorption of the complete molecules only occurs in short-chain films, and (iii) better ordered SAMs exhibit a higher stability toward electron irradiation.

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Electron mean free path in the partial electron yield acquisition mode*

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In the partial electron yield (PEY) acquisition mode commonly used in X-ray absorption spectroscopy both elastically and inelastically scattered electrons contribute to the signal. Compared to X-ray photoelectron spectroscopy (XPS) the majority of inelastic scattering events will not result in a signal reduction because the scattered electrons will still have a kinetic energy in the acquisition range of the spectrometer. The related values of mean free path (MFP) should be, therefore, noticeably larger than the well-known inelastic mean free paths (IMFP) for electrons of definite kinetic energy. We have performed XPS and near edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements for well-defined self-assembled monolayers of alkanethiols (AT) $CH_3(CH_2)_nSH$ on gold metal surfaces. The variation of the alkyl chain length (n = 10 - 26) and, subsequently, the film thickness enabled us to estimate the MFP for both the XPS and NEXAFS acquisition modes. In the case of NEXAFS spectroscopy the PEY signals related to the pre-region and the C 1s absorption egde are provided by Au 4f photoelectrons of the substrate and C_{KLL} Auger electrons of the AT monolayer, respectively. Assuming an exponential attenuation of the Au 4f and C_{KLL} intensities by the AT overlayer and taken a clean, well-sputtered Au sample as a reference, the MFPs of the Au 4f and C_{KLL} electrons in the PEY acquisition mode can be extracted from the series of NEXAFS spectra. In agreement with the expectations, the obtained effective MFPs exceed the respective values for elastically scattered electrons with the same kinetic energy. Furthermore, the MFP for the inelastically scattered C_{KLL} Auger electrons increases with decreasing retarding voltage, which correlates with the increasing contribution of the inelastically scattered electrons in the acquired PEY signal.

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High-resolution electron spectroscopy of atomic barium *

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Barium is a good example of strong correlation effects in the photoionization process. Strong configuration interaction (CI) has to be taken into account for the description of the ground state (6s^2 ^{1}S$_0$) and also for the final state. In the former, mixing with the 6p^2, 5d^2 and 4f^2 states and in the latter, mixing with the 6s5d, 6p^2, 5d^2, 6p4f and 4f^2 states is important.
To examine the influence of CI, we performed high-resolution measurements of the 4d photoelectron and NOO, NOV Auger electron spectra at beamline 10.0.1 of the Advanced Light Source. A photon bandwidth of 40-50 meV was used at 131.2 eV photon energy. The electron spectra were collected using a Scienta SES-200 hemispherical analyzer using an electron energy resolution of 40-50 meV. A resistively heated metal vapour oven (operated at 540-590^{o}C) was used to generate an effusive beam of Ba atoms.
The 4d photoelectron spectrum is mostly dominated by final ionic state configuration interaction (FISCI) resulting in a manifold of correlation satellites. Additionally, the 4d$^-1$ 6s7s, 4d$^-1$ 6s6p and 4d$^-1$ 6s4f shake-up satellites are observed with an intensity of approx. 30% of the FISCI satellites.
Through a comparison of our measurements with relativistic Hartree-Fock calculations most of the observed lines can be assigned, which leads to a better understanding of the influence of electron correlations on the photoionization process.

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New Experiments in Spectro-Microscopy by Means of Photoelectron Time-Of-Flight Analysis

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A new method for energy-selective imaging using a conventional photoemission electron microscope (PEEM) was performed in a relatively simple way. A modified commercial PEEM (FOCUS IS-PEEM) combined with a special delay-line device as x,y,t-resolving detector [1] served as the basic arrangement for spectro-microscopy. In order to analyze the energy distribution of photoelectrons in PEEM one can measure the time of flight of the electrons passing a drift section, referenced to the time structure of the synchrotron radiation from an electron storage ring (here: BESSY-I, PM-III). At electron kinetic energies as low as 20eV within the drift region a spatial resolution of about 100nm has been obtained. Fast counting electronics (instead of a camera) delivers an image for real-time monitoring on an oscilloscope screen. A time resolution of about 500ps has been obtained with the potential of further improvement. The spatial resolution of the delay-line detector is about 50 microns in the image plane being equivalent to 1000 pixels in the image diagonal. Direct photoemission from the W-4f core level of a W(110) single-crystal sample was observed at several photon energies. Additionally, we demonstrate the energy selective imaging by measurements at a structured Fe/Si-sample. Finally, we will show how to perform experiments to investigate the local environment of atomic photoemitters on solid surfaces using photoelectron holography [2] with circularly polarized light by means of the TOF technique.
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Angular Resolved Measurements of the Spin-Orbit Branching Ratio in Soft-X-Ray Photoelectron Spectroscopy from W(110)

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The spin-orbit branching ratio (B.R.), that is the intensity ratio of the lines of a spin orbit split doublet, is one of the quantities that can be measured very easily in photoemission experiments. Initially it was defined for angular integrated photoemission or photoabsorption experiments, being equivalent to a measurement at the magic angle 54.7°. Its statistical value is simply determined by the multiplicity of the initial states. In photoemission from solids or adsorbates the situation changes, because scattering effects have to taken into account and the observation is restricted to the half space above the sample, so structural information can be extracted from B.R. measurements. We have measured the spin-orbit branching-ratio in the photoemission from the 4f state of an W(110) single-crystalline sample. The measurements were carried out in UHV using circularly polarized synchrotron radiation from BESSY-I (Berlin). We have measured angular resolved photoemission across a large sector in k-space by use of an analyser mounted at a two-axes-goniometer. The results show that the branching ratio in angular resolved photoemission deviates significantly from the statistical value. In emission from solids photoelectron diffraction plays an important role. It causes the angular distribution being modulated by diffraction features. Obviously such changes of the angular distribution will give rise to changes in the branching ratio, too. The observed deviations are closely connected with the occurrence of dichroism in the angular distribution, that are differences in the intensities if the polarization of the photons is changed. Various atomic and solid state effects have to be taken into account for a better interpretation of the observed results.
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High-resolution electron-energy-loss spectroscopy in the study of organic thin film growth*

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High-resolution electron-energy-loss spectroscopy (HREELS) is a well established method for the investigation of adsorbates. In these systems information on the surface bonding and adsorbate structure is obtained from frequency shifts with respect to the gaseous phase and from the relative intensities of differently polarized dipole-active vibrations according to the surface selection rule [1], respectively.Nowadays, organic multilayer films receive increasing interest because of their possible technical applications such as tayloring of surface properties, molecular electronics, resists, or sensors. The study of multilayer films by HREELS, on the other hand, has been impeded so far by the following facts:
- The growth mode and thus the structure of organic films often changes with coverage.
- In many cases organic multilayer films are disordered.
- Only in ordered samples can dipole-active vibrations be identified by their characteristic angular spectral dependence.
- There is uncertainty about the distance from the surface at which the selection rule breaks down.

Recently, we have proposed a new method that allows to identify dipole-active vibrations from an analysis of multiple scattering processes in disordered multilayer molecular films [2]. While this method also allows to detect overtones and thus resonant processes in multilayer films, the resulting assignment of the vibrational bands in HREELS is essential to the study of the growth of organic molecular films. It will be shown in this contribution how the thickness dependences of dipole and impact scattering differ. Together with the angular distribution of dipole scattering [3] this can be exploited to monitor changes in growth mode during film deposition. Further perspectives for the investigation of thin film growth are outlined.

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Surface Core Level Shifts of Clean and Oxygen Covered Ru(0001)

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Surface core level shifts (SCLS) measured at high resolution, as is now available at third generation synchrotron sources, can contribute valuable information on the charge rearrangements induced by the surface situation for clean surfaces, and by the presence of adsorbates. Even if measured with high resolution, the disentanglement of the observed shifts into contributions of initial state (charge redistribution in the ground state, including bonding) and of final state (charge redistribution in the core-ionized state, in particular screening changes) effects is difficult. Such an interpretation is possible if equally accurate and reliable calculations are available.
We have performed High Resolution XPS experiments of the Ru(0001) surface, either clean or covered with well-defined amounts of oxygen. For the clean surface we detected two distinct components in the $Ru3d_{5/2}$ core level spectra, for which a definite assignment was made using the High Resolution Angle-Scan Photoelectron Diffraction approach. The first principles all electron density functional slab calculations (LAPW code WIEN97, PBE-GGA) are in very good agreement with our experimental results. For the (2x2), (2x1), (2x2)3O and (1x1) oxygen structures we found Ru $3d_{5/2}$ core level peaks which are shifted up to 1 eV. Again, very good agreement with the corresponding calculations results. Since the latter permit the separation of initial and final state effects, our coupled results give valuable informations for the understanding of bonding and screening at the surface otherwise not accessible in the measurement of the core level energies of the adsorbate. We also report and discuss peak shapes obtained from detailed fitting procedures.

Three-Dimensional Imaging of Ions and Electrons Produced in Photoexcitation *

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Recently, novel imaging techniques have been developed that enable the simultaneous determination of the complete momentum vectors of several electrons and ions emerging from atomic or molecular ionisation or fragmentation reactions [1]. The method relies on the projection of all electrons and ions onto position and time resolving multi-hit capable detectors by means of electric and magnetic guiding fields. From the times of flight and the hitting positions the trajectories of the particles are restored and their initial momenta are calculated. These instruments, so-called reaction microscopes, enabled a new generation of kinematically complete experiments that monitor the entire many-particle finale state yielding unprecedented information on the dynamics of many-particle quantum-systems.In the talk the technique is described in some detail and selected results are presented for photoionisation at third generation synchrotron radiation facilities, for break-up reactions in intense virtual photon fields of highly-charged relativistic ions as well as on multiple ionisation of atoms and molecules in intense, femtosecond laser fields. Future perspectives are discussed like the investigation of multi-photon processes at the TESLA-FEL in Hamburg or photoionisation of atoms and molecules in the presence of strong laser fields.

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Synchrotron Radiation Photoemission Study on the Growth of Gd Film over Ni(110) Surface*

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The growth of Gd film on Ni(110) surface has been studied by synchrotron radiation photoemission spectroscopy and XPS techniques. The results demonstrated that in the coverage range of 0-0.22nm, Gd4f core level showed a single-peak(s-p) structure, but when the coverage is larger than 0.22nm, the Gd4f transition turned gradually into double-peak(d-p) and a d-p structure with 2.3eV separation was formed at 1.51nm. Similar phenomenon was observed in the Gd4d XPS spectra. It is suggested that the s-p structure of Gd4f emission comes from a uniform Gd film at Gd(I) state grown in layer-by-layer mode, while the d-p structure may be derived from the Gd film at Gd(II) state grown in cluster mode and the Gd atomic clusters may exhibit different electronic states from Gd metal owing to the existence of diverse surface defects and dangling bonds. The Gd4f d-p structure evolved into s-p feature on annealing at 600K, implying that Gd clusters are unstable thermodynamically.

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Oxidation of Gd Films on Ni(110) Surface Studied by Photoemission*

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Soft X-ray synchrotron radiation photoemission and X-ray photoelectron spectroscopy (XPS) have been used to study the interaction of oxygen with Gd overlayers grown in situ on Ni(110) surface and with the Gd-Ni composite film. The 3.7 nm-thick Gd film containing Gd clusters exhibited a large primary adhesive coefficient for oxygen owing to the existence of surface defects and dangling bonds. The high binding energy (BE) peak in the double-peak feature of Gd4f emission attenuated with the increase of oxygen exposure and almost disappeared when the sample was annealed at 800 K after a 50L coverage suggesting that the surface oxidation reaction promotes the decomposition of Gd clusters. The O1s XPS spectra exhibited only one peak attributed to lattice oxygen at 529.6eV in the range of 0-50L exposure.

Over the surface of Gd-Ni composite film prepared by slight oxidation and high temperature (1000 K) annealing treatment of 0.63 nm Gd film, the adsorption of oxygen resulted in the surface segregation and oxidation of Gd component. Two kinds of oxygen species, the chemisorbed O$^-$ ion and lattice oxygen, were detected implying that there are two kinds of active sites on the Gd-Ni composite film. High temperature annealing of the oxidized Gd-Ni film led to the microcrystallization of Gd oxides and the transformation of chemisorbed oxygen to lattice one. The oxidation mechanism of Gd film as well as the nature and evolution of the surface oxygen species are discussed.

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Comparison of k-resolved single-particle spectra of XRu_2Si_2 (X=La, Th, Ce, U).

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The k-resolved single particle excitations, as determined by angle-resolved photoemission spectroscopy (ARPES), are compared and contrasted for, $LaRu_2Si_2$, $ThRu_2Si_2$, $CeRu_2Si_2$, and URu_2Si_2, isostructural layered compounds with differing nominal f-occupations of f^0, f^0, f^1, and f^2, respectively. ARPES measurements include 4d and 5d-edge resonant photoemission to distinguish f-character and Fermi-edge intensity mapping of Fermi surface contours. Comparison to RLAPW band structure calculations [1] shows very good agreement with the d-band structure away from E_F and with the Fermi surfaces of the f^0 compounds. Discrepancies in the near E_F region of the Ce and U compounds highlight k-dependent effects of f-correlation and f-d hybridization. High-resolution ARPES at the f-resonances allows detailed measurement of single-particle lineshapes that can be compared to predictions of the Anderson lattice model.

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